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PREPARATION OF FLUORINE-CONTAINING COMPOUNDS

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WRIGHT AIR DEVELOPMENT CENTER

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AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared at the University of Florida under Contract Nonr 580(03); NR 356-333 for the Office of Naval Research. The work was supported in part by the United States Air Force under Project No. 7340, "Rubber, Plastic, and Composite Materials", Task No. 73404 "Synthesis and Evaluation of New Polymers". The contract work was administered by the Chemistry Branch of the Office of Naval Research and monitored by Lt. A. M. Lovelace of the Materials Laboratory, Directorate of Research, Wright Air Development Center.

This report summarizes the work completed from January 1954 to May 1956.

WADC TR 56-234

ABSTRACT

Part of the objective of this program is the preparation or attempted preparation of new fluorine-containing chemical species by the Simon's electrochemical process. The results of numerous operations in a variety of cells are summarized. Studies have been made with some of the resulting materials in order to find unique reactions of these materials and thereby new compounds exhibiting the chemical and thermal stability associated with fluorocarbons.

The preparation, pyrolysis or thermal reactions of certain simple fluorocarbon sulfides with fluorocarbon olefins are described. The sulphides are CF_3SF_5, $C_2F_5SF_5$, $(CF_3)_2SF_4$ and $(C_2F_5)_2SF_4$. The olefins involved were $CF_3CF=CF_2$, and $CF_3N=CF_2$.

The synthesis and properties of fluorocarbon derivatives having hetero atoms such as oxygen or nitrogen in the principal carbon chain of the molecule have been studied. It has been shown that a perfluoro compound having an alternating chain C-O-C-N-C cannot be synthesized directly from the organic analogue. When prepared indirectly, however, such a chain is chemically and thermally stable. The compounds $(CF_3)_2NCOF$, $CF_3N=CF_2$, and $(CF_3)_2NCF_2COOH$, which are the N-hetero analogues respectively of $(CF_3)_2CFCOF$, $CF_3CF=CF_2$, and $(CF_3)_2CFCF_2COOH$, are discussed. The

pyrolysis of a compound having C-C, C-O, and C-N bonds is described. Preparation of a new and unexplored class of compounds, the perfluoroamides, and the synthesis of a possible intermediate in the preparation of the difunctional acid $O(CF_2COOH)_2$ are mentioned.
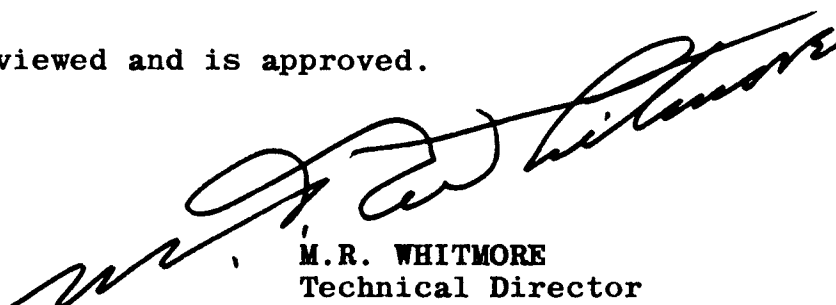
Reaction of fluorocarbon olefins and chlorofluoroolefins has produced sulfur-containing fluorocarbon derivatives stable to aqueous alkali. Preparations and reactions of perfluoroalkyl amidines, $R_FC(:NH)NH_2$, and perfluoroalkyl triazines, $(R_FCN)_3$, have been studied. The reaction of polytetrafluoroethylene with sulfur or selenium under pyrolytic conditions produces a fusible polymer containing no sulfur.

Efforts to use potassium and sodium vapor as a reaction medium for fluorocarbon synthesis have not been successful. Fluorine exchange between metal fluorides and fluorocarbon olefins has been studied. Exchange was generally accompanied by decomposition. It was found that the reactor packing determined the nature of the products obtained from the oxidation of C_3F_6.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M.R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

TABLE OF CONTENTS

LIST OF TABLES

WADC TR 56-234

I. SUMMARY OF ELECTROCHEMICAL SYNTHESES IN HYDROGEN FLUORIDE

Part of the program of this work has entailed the electrochemical preparation of specific fluorine-containing materials to study their properties and potential in further syntheses. To do this, a number of electrochemical cells (Simon's type) were constructed and operated. These had a nominal current (D.C.) capacity of 100, 50, and 20 amperes, respectively. These units all have the following components, namely, (a) cell container with electrode pack, (b) overhead condenser to reflux effluent HF, (c) refrigeration unit to cool condenser and cell, (d) cell liquid level indicator, (e) devices for adding HF and organic substance to the cell, (f) a controlled source of current and potential and (g) a train for collecting products. In operating these units, a minimum voltage is used compatible with reasonable currents, cell temperatures, cell concentrations, and the ability of the refrigeration and product collection systems to perform their functions adequately.

The following table summarizes all the electrochemical operations performed on this contract.

TABLE I

SUMMARY OF ELECTROCHEMICAL OPERATIONS

Starting Material	Amount (gms)	Products and/or Boiling Range if Unidentified	Amount Ea. in Grams
$(C_2H_5)_3N$	675	$(C_2F_5)_3N$	510
		Non-condensible at -70°C.	780
		Other materials above -70°C.	340
$(C_2H_5)_2NCHN(C_2H_5)_2$	2000	Non-condensible at -70°C.	1560
		$17-18^{\circ}$C	243
		$(CF_3)_2NC_2F_5$ 21°C	165
		$33-35^{\circ}$ C	155
		$(C_2F_5)_2N$ CF_3 46°C	855
		Intercuts	232
CH_3OCH_2COF	601	CF_4, C_2F_6	92
		CO_2, COF_2	50,19
		CF_3OCF_3 (B.P. -61°C.)	17
		CF_3COF (B.P. -59°C.)	43
		$16.5-18.5^{\circ}$C	28
		$20-22^{\circ}$C	14
		Intercuts	30
$(CH_3)_2S$	810	CF_4, SF_4, C_2F_6, $(SF_6?)$	840
		-49 to -21°C	42
		CF_3SF_5	1310
		-20 to 15°C	45
		$(CF_3)_2SF_4$	92
		Base extractable materials	340
C_4H_9COCl	1320	Below -78°C.	Not recorded
		-8 to -6°C	25
		C_4F_{10}	70
		$8-29^{\circ}$C	25
		Cyclic $C_5F_{10}O$	175
		C_4F_9COF	100
		Other acid fluorides	35

WADC TR 56-234

2

Starting Material	Amount (gms)	Products and/or Boiling Range if Unidentified	Amount Ea. in Grams
$(CH_2)_4(COCl)_2$	1857	Below $-78^{\circ}C$.	Not recorded
		to $25^{\circ}C$.	268
After esterification		Unidentified esters	120
		$H(CF_2)_4COOC_2H_5$	75
		$(CF_2)_4(COOC_2H_5)_2$	80
$(C_2H_5)_2O$	891	Cleavage products	Not recorded
		$(C_2F_5)_2O$	433
		Other fluorine-containing materials	194
$(CH_3)_2NCOCl$ High Initial Conc.	1423	Cleavage products	1750
		$(CF_3)_2NCOF$	154
$(CH_3)_2NCOCl$ Low Initial Conc.	2175	Cleavage products	2105
		$(CF_3)_2NCOF$	965
$(CH_3)_2NCOCl$ Low Initial Conc.	1930	Cleavage products	Not trapped
		$(CF_3)_2NCOF$	776

The following syntheses were done in the nominally 20 ampere cell. (Material boiling below $-78^{\circ}C$ not recorded).

Starting Material	Amount (gms)	Products and/or Boiling Range if Unidentified	Amount Ea. in Grams
$CF_3CON(CH_3)_2$	569	CF_3COF	65
		$(CF_3)_2NCOF$	137
		$(CF_3)CON(CF_3)_2$	48
		Others	129
$(CH_3)_2NSO_2Cl$	157	SOF_2, SO_2F_2	21
		Others	21
$(C_2H_5)_2NCOCl$	595	$(CF_3)_2NCOF$	73
		$CF_2CF_2OCF_2N-C_2F_5$	365
		Mixture boiling to $200^{\circ}C$	220
		Others	73

WADC TR 56-234

3

Starting Material	Amount (gms)	Products and/or Boiling Range if Unidentified	Amount Ea. in Grams
$(CH_3)_2NCON(CH_3)_2$	196	CF_3NCOF	110
		$(CF_3)_2NCON(CF_3)_2$	10
		Others	27
$CH_3CON(CH_3)_2$	403	No identifiable products $6-71^{\circ}C$	106
$CH_3CH(OCH_3)_2$	250	-56° to $40^{\circ}C$ (No flats) Tar in cell	35
$O(CH_2CH_2)_2NCOF$	604	$(CF_3)_2NCOF$	35
		$O(CF_2CF_2)_2NCOF$ (b.p. $45-48^{\circ}$)C	30
		Unidentifiable 0 to 240° C	300
$(C_2H_5)_2S$	270	-54 to $11^{\circ}C$	49
		11 to $12^{\circ}C_2F_5SF_5$	203
		12 to $68^{\circ}C$	50
		$(C_2F_5)_2SF_4$ B.P. $68.0^{\circ}C$	26
$(CH_3)_2NCH_2COOCH_3$	54	$(CF_3)_2NCF_2COF$ b.p. $24-25^{\circ}C$	7
$(CH_3)_2NCH_2\overset{O}{\overset{\|}{C}}N(CH_3)_2$	379	$(CF_3)_3N$	16
		$(CF_3)_2NCOF$	75
		$(CF_3)_2NCF_2COF$	21
		$81^{\circ}C$ (cyclic)?	13

II. PYROLYSES AND THERMAL REACTIONS OF SOME SIMPLE FLUOROCARBON SULPHUR COMPOUNDS

The main effort of this portion of the contract work was to study the thermal or pyrolytic properties of various fluorocarbon sulfides and their thermal reactions with certain unsaturated fluorocarbon compounds.

The pyrolytic properties of the fluorocarbon sulfides such as CF_3SF_5, $(CF_3)_2SF_4$, and $C_2F_5SF_5$ were studied by passage of these substances in the vapor phase at atmospheric pressures and high temperature through a nickel tube packed with nickel or NaF pellets. The thermal reactions were studied using generally equimolar quantities of reactants in the above (flow) system or in a stainless steel reaction vessel (Static) heated until the pressure changes indicated a reaction (or not).

A. CF_3SF_5 was found to decompose over nickel to the extent of 2% by weight at about 450°C. and 20% at 520°C. The products were mainly C_2F_6 and SF_4 (and possibly other sulfur fluorides). The nickel packing was attacked but not extensively. $(CF_3)_2SF_4$ was found to decompose 40% by weight at 500°C over NaF pellets in a nickel tube. Under these conditions the main products were C_2F_6 and SF_4 with traces of CF_4 and some material boiling between -15 and 0°C later shown to be mostly CF_3SF_3.

$C_2F_5SF_5$ decomposed 100% at 500°C. to yield C_2F_6, C_4F_{10}, SF_4 and other sulfur fluorides.

Flow rates for all pyrolytic experiments were between 0.13 and 0.30 grams per minute with contact times in the maximum heat zone of the reaction tube estimated to be in the order of 15 to 30 seconds.

The reactions of the fluorocarbon sulphur compounds can be summarized by the following equations:

TABLE II

SUMMARY OF THE REACTION OF SIMPLE FLUOROCARBON SULPHUR COMPOUNDS

System	Reactants		Products
1 Flow	$CF_3SF_5 + CF_3CF = CF_2$	$\xrightarrow{520^\circ C}$	$C_2 + C_4$ to C_8 fluoro-carbons and S fluorides.
2 Static	$CF_3SF_5 + CF_3CF = CF_2$ (yields of C_5 and C_6 higher at expense of C_4).	$\xrightarrow{423^\circ C}$	C_4 to C_8 fluorocarbons
3 Flow	$CF_3SF_5 + CF_3N = CF_2$	$\xrightarrow{520^\circ C}$	$(CF_3)_3N + SF_4$ 58%.
4 Flow	$CF_3SF_5 + (CN)_2$	$\xrightarrow[\text{to } 550^\circ C]{520^\circ C}$	CF_3CN + other products not isolatable. Yield poor.
5 Flow	$CF_3SF_5 + CF_3CN$	$\xrightarrow{520^\circ C}$	Small yield CF_3SF_3 About 20%
6 Flow	$(CF_3)_2SF_4 + CF_3CF=CF_2$	$\xrightarrow{512^\circ C}$	C_5F_{12} 57%
7 Flow	$(CF_3)_2SF_4 + CF_3N = CF_2$	$\xrightarrow{520^\circ C}$	Olefin unreacted $CF_4 + CF_3SF_3$ – 35% $C_2F_6 + SF_4$ – 65%
8 Static	$C_2F_5SF_5 + CF_3CF = CF_2$	$\xrightarrow{390^\circ C}$	C_4 to C_{10} fluorocarbons
9 Static	$C_2F_5SF_5 + CF_3N = CF_2$	$\xrightarrow{375^\circ C}$	$(CF_3)_2N\ C_2F_5$ 46% + other products not isolatable.

WADC TR 56-234

6

In reactions 1, 2, and 6 part of the C_5F_{12} fraction isolated contained neo-C_5F_{12}, a white crystalline solid melting at 78.3°C. in a sealed melting tube. On standing it converts to a viscous glass that can be recrystallized by cooling to lower than -50°C.

A melting point was determined for pure $(CF_3)_3N$. It was -114 ± 0.7°C. Its vp curve fits the equation

$$Log_{10}P_{mm} = \frac{1250}{T°K} + 7.61$$

between -80° and -10°C. The calculated b.p. is -10.9 ± 0.1°C, ΔH_v 5680 $\frac{Cal}{mole}$ and Trouton's constant 21.6.

III. A STUDY OF THE SYNTHESIS AND PROPERTIES OF PERFLUORO COMPOUNDS CONTAINING HETERO ATOMS IN THE MAIN CHAIN

The object of this research has been the incorporation of hetero atoms, especially N and O, into the backbone of fluorocarbon molecules.

It was found early in the program that extended alternating chains of the type C-X-C-Y-C, where X and Y are hetero atoms, cannot be prepared directly by the electrochemical process. Thus, neither $(C_2H_5)_2NCH_2N(C_2H_5)_2$ nor $O(CH_2COCl)_2$ gave more than traces of the perfluoro analogs. Subsequent work has shown that once made, such chains have the chemical and thermal stability usually associated with fluorocarbons, and the direct preparation of such a chain fails not because of any inherent instability in this arrangement but because of the instability of the organic precursor during reaction conditions. For instance, $\overline{CF_2OCF_2N}\text{-}\overline{CF_2}$ with a CF_3 group on N, is unaffected when refluxed with concentrated acids or bases, and is only about 10% decomposed at $650^{\circ}C$., with a calculated contact time of 9 minutes.

In order to obtain the desired end by indirect synthesis, some reactive fluorocarbon derivatives containing hetero atoms were prepared. The first of these was $(CF_3)_2NCOF$, bis-(trifluoromethyl) carbamyl fluoride, which has been made from $(CH_3)_2NCOCl$ and half-a-dozen other starting materials, any compound having the formula

WADC TR 56-234

$(RCH_2)_2N-CO-M$, where M is halogen, hydrogen, or nitrogen, being likely to give the carbamyl fluoride as one product. It was found that the free acid $(CF_3)_2NCOOH$, as well as most of its derivatives, is apparently unstable under ordinary conditions, and all attempts to prepare derivatives other than esters, of which several have been made, resulted in complete destruction of the molecule.

Pyrolysis of the carbamyl fluoride, either in a flow system at 550-600°C or merely by heating in a stainless steel vessel at 375-400°C, gave excellent yields of the azomethine $CF_3N=CF_2$, which is formally analogous to the carbon-chain compound perfluoropropene, $CF_3CF=CF_2$, although different in its chemical reactions. When this compound was heated with free radical sources such as CF_3I or CF_2Br_2, as well as with CF_3CN or HCN in the presence of BF_3, no addition to the C=N double bond took place. A small amount of polymeric material was obtained from these runs whose properties – insolubility in all solvents tested except concentrated acids, and high thermal stability – were concordant with the homopolymeric chain $(-N-CF_2-)_n$, but the actual structure of the material has not been established. The azomethine did react with CF_3SF_5 in an apparent free radical reaction to give $(CF_3)_3N$, as detailed in Section II.

Use of higher carbamyl chlorides in the electrochemical process led not to homologs of $(CF_3)_2NCOF$, but to cyclic compounds of the type R-CF – O   where R may be fluorine or perfluoroalkyl, depending
         | |
        CF_2 CF_2 on the starting material. These compounds have
          \   /
           N-R

excellent chemical and thermal stability. As they contain C-C, C-N, and C-O bonds, a study was made of the mode of thermal decomposition of $\overline{CF_2OCF_2N}\overset{\overset{\displaystyle CF_3}{|}}{C}F_2$. Results indicate that at about 700°C., COF_2 is eliminated and compounds containing carbon-nitrogen unsaturation are formed.

Although $(CF_3)_2NCOOH$ is unstable, insertion of a CF_2 group between the nitrogen and carboxyl affords reversion to normal stability. The resulting acid $(CF_3)_2NCF_2COOH$, which is the N-hetero analog of perfluoro isovaleric acid, is both the first reported fluorocarbon amino acid and the first branched chain fluorocarbon acid to be isolated in a pure state. Derivatives made so far indicate that it will be possible to develop a whole gamut of reactions for this hetero acid, as has been done for the usual fluorocarbon acids. Presence of the branched chain and absence of a beta fluorine should provide some interesting variations, as a reaction analogous to the following;

$$CF_3CF_2CF_2COONa \longrightarrow CF_3CF{=}CF_2$$
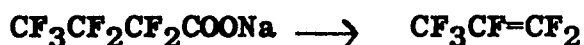
is manifestly impossible.

Another entirely new class of compounds of which representatives have been synthesized is the perfluoroamide. Two which have been identified are $CF_3CON(CF_3)_2$ and $(CF_3)_2NCON(CF_3)_2$. No study has yet been made of their chemical behavior.

The most complex molecule containing hetero atoms to be directly synthesized electrochemically in this work is the compound

WADC TR 56-234

$O(CF_2CF_2)_2NCOF$. Isolation of this compound demonstrates that it is at least possible to produce some rather complex molecules by this method, though with present knowledge of the process the yields are apt to be very small. The $O(CF_2CF_2)_2NCOF$ was made as a possible route to $O(CF_2COOH)_2$, and feasibility of subsequent steps in the synthesis has not yet been determined.

IV.

A. A STUDY OF THE PHYSICAL ENVIRONMENT FOR FLUOROCARBON REACTIONS

Attempts have been made to use alkali metal vapors as a reaction medium for carrying out fluorocarbon reactions in the temperature range 100-450°C. Sodium and potassium have been employed for this purpose. The reactants studied were CF_4, SF_6, CF_4-SF_6, CF_3Br, and CF_3I. The reactant or reactants, diluted with an inert gas, were passed through a reactor filled with the vapor of the alkali metal. Operating pressures were either 760 mm. of mercury or 10 mm. of mercury. The products were trapped in liquid air and distilled. No materials other than the starting material, carbon, and the alkali metal fluoride or sulfide were recovered.

B. STUDIES ON FLUORINE EXCHANGE REACTIONS AND POSSIBLE CATALYSTS FOR FLUOROCARBON REACTIONS

Preliminary experiments studying the exchange reactions between metal fluorides and fluorocarbons* have been carried out.

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*This work is being carried out at the Oak Ridge National Laboratory with the aid of an Oak Ridge Institute of Nuclear Studies Fellowship for Mr. T. A. Gens. The work at the Laboratory is under the supervision of E. R. Van Artsdalen and A.R. Brosi.

The isotope F^{18} was used in this work. The long-range goal of the work is to find fluorides which will act as catalysts for fluorocarbon reactions.

F^{18} was produced by the two nuclear reactions:

$$(1) \quad _{3}Li^{6}(n; \alpha)_{1}t^{3}$$

$$(2) \quad _{8}O^{16}(t; n)_{9}F^{18} \quad .$$
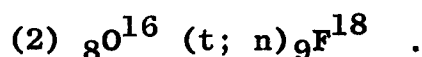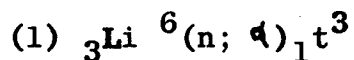
Equimolar mixtures of lithium fluoride and aluminum oxide were bombarded in a reactor. The products were then exchanged with anhydrous hydrogen fluoride to give HF^{*} which was then exchanged with the appropriate metal fluoride.

The metal fluoride containing F^{18} was placed in a boat within an Inconel tube heated by an electric furnace. The tube was connected to a glass loop system through which the fluorocarbon was circulated. The loop passed through a counting chamber surrounded by a NaI crystal so that radioactivity in the gas phase was monitored. A mercury manometer was used to follow pressure changes in the system.

Twenty-six runs, generally qualitative in nature, have been carried out. Exchange between C_3F_6 and NaF^{*} began at 200-300°C. and increased with temperature. The exchange was strongly influenced by the rate at which the salt was heated. As the temperature was increased a pressure increase was noticeable at about 400°C.; consequently these preliminary experiments probably point to decomposition accompanied by exchange. CF_4 and NaF^{*} showed a little exchange at 665°C.; however, no pressure change could be detected. After the experiments, the sodium fluoride showed a deposit of carbon. CrF_2^{*}-C_3F_6 showed no exchange and no pressure increase up

WADC TR 56-234

to 500°C. C_3F_6-CuF_2* showed no pressure change or exchange up to 335°C. The system $CF_3N{=}CF_2$ - NaF* showed exchange and pressure effects at considerably lower temperatures - about 250°C. CsF* - C_3F_6 showed tremendous exchange plus a pressure decrease at higher temperatures.

At this point, it is clear that sodium fluoride will exchange with fluorocarbon olefins or their decomposition products at moderate temperatures. The exact nature of these reactions is not known at this time.

C. **SEARCH FOR MATERIALS WHICH WILL REACT DIRECTLY WITH FLUOROCARBONS**

Attempts were made to react CF_4 with oxygen, carbon monoxide, and carbon dioxide using a "catalyst" of silica gel or cupric oxide. The results were negative up to 400°C. Similar studies were carried out in the presence of a zinc oxide surface. Again the results were negative; however, it was observed that adsorption of oxygen on the zinc oxide stopped subsequent adsorption of CF_4 on the surface. The oxidation of CF_3H was studied with a cupric oxide surface at temperatures up to 400°C. Products were CO_2 and water with some of the cupric oxide converted into fluoride. When water was one of the reactants, silicon tetrafluoride was also obtained.

The oxidation of C_3F_6 in the presence of sodium fluoride, cupric oxide, or silica gel has produced interesting results. Treatment of C_3F_6 alone over sodium fluoride at 500°C. resulted in traces

WADC TR 56-234

of both high and low boiling materials; however, the majority of the olefin was unchanged. Treatment with oxygen over sodium fluoride at 400–500°C. gave good yields of CF_3COF and COF_2. No carbon dioxide was found. The olefin and cupric oxide yielded traces of neutral materials plus carbon dioxide. Oxygen and C_3F_6 with cupric oxide at 400–500°C. produced carbon dio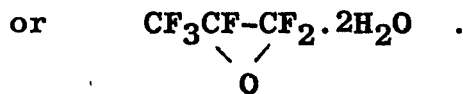xide and small amounts of neutral liquids boiling from 0°C. to + 80°C. These liquids could not be separated by distillation. Chromatography proved the presence of eight components. When cupric oxide was used in the oxidation, no acidic materials were found.

All runs with C_3F_6 – oxygen over copper oxide yielded a small quantity of white crystals. The crystals, after dehydration with phosphrous pentoxide, gave a low boiling liquid. These crystals are believed to be either

$$CF_3CF - CF_2 \cdot H_2O \qquad \text{or} \qquad CF_3CF-CF_2 \cdot 2H_2O$$
$$\underset{O \ - \ O}{| \qquad \quad |} \qquad\qquad\qquad \underset{O}{\diagdown \ \diagup}$$
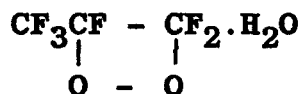
$$\text{(I)} \qquad\qquad\qquad\qquad \text{(II)}$$

The chemical and physical evidence available at this time favors Structure I.
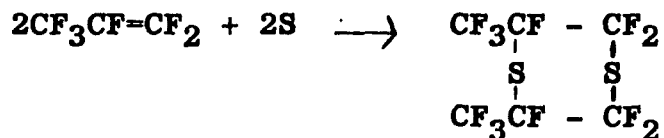
This work has shown that the surface employed for the oxidation of fluorocarbon olefins exerts a profound influence on the end-products of the reaction. Oxidation over sodium fluoride gave acidic products. Oxidation over cupric oxide gave neutral materials.

WADC TR 56-234

V.

A. REACTION OF FLUOROCARBON OLEFINS WITH SULFUR

1. $CF_3CF=CF_2$.- Previous work in this laboratory has indicated the formation of a stable, sulfur-containing fluorocarbon derivative from the reaction of $CF_3CF=CF_2$ with sulfur. This compound appears to be heterocyclic with two sulfur atoms in the typical 1,4 dithiane structure.

$$2CF_3CF=CF_2 + 2S \longrightarrow \begin{array}{cc} CF_3CF - CF_2 \\ | \quad\quad | \\ S \quad\quad S \\ | \quad\quad | \\ CF_3CF - CF_2 \end{array}$$

This structure is stable to hydrolysis and inert in most chemical reactions.

2. $CF_2=CFCl$.- Trifluorochloroethylene with elementary sulfur in a sealed steel reaction vessel at temperatures in the range 250-380°C produced, in addition to the dimer of the olefin, a compound boiling at 85-91°C and a compound boiling at 137°C. These compounds are stable to prolonged refluxing with aqueous alkali.

3. $CF_2=CF_2$.- The dimerization reaction of this olefin predominated when it was heated in the presence of sulfur. No sulfur-containing products were isolated.

4. 1,2 dichlorohexafluorocyclopentene.- No reaction with sulfur after 18 hours at 300°C.

5. $\underline{CF_2-CF_2CF=CF}$.- Hexafluorocyclobutene did not react after

20 hours at 300°C with sulfur. Reaction at 350°C for 63 hours produced considerable decomposition to sulfur fluorides hydrolyzable in alkali and to carbon disulfide.

6. C_7F_{14} (reported structure - $CF_3(CF_2)_4CF=CF_2$).- No reaction between this olefin and sulfur was observed at 300°C. At 385°C, C_7F_{14} reacted explosively to rupture the sealed, heavy walled glass reactor. At 350°C, the reaction was controllable but produced only compounds hydrolyzable in alkali.

B. REACTIONS OF FLUOROCARBON DERIVATIVES WITH COMPOUNDS CONTAINING SULFUR

The reaction of $CF_3CF=CF_2$ with S_2Cl_2 was studied at 260°C in a steel vessel. No sulfur-containing fluorocarbon derivative resistant to alkali was produced. A chlorine addition product, $CF_3CFClCF_2Cl$, and a chlorofluorocarbon resulting from addition of chlorine and substitution of fluorine by chlorine, $CF_3CCl_2CF_2Cl$, were obtained.

The compound $CF_3CFClCF_2Cl$ did not react with sulfur in a sealed tube at 400°C; a combination of sulfur and zinc sulfide with this olefin under the same conditions produced an explosion.

C. PERFLUOROALKYL AMIDINES AND RELATED COMPOUNDS

A member of perfluoroalkyl amidines, $R_FC(:NH)NH_2$ have been made by the reaction of liquid ammonia with fluorocarbon nitriles. N-alkyl substituted perfluoroalkyl amidines were formed by a similar method using primary or secondary amines in place of ammonia. Mercury and silver salts and acid addition compounds of the perfluoroalkyl amidines have been prepared. Perfluoroalkyl thioamides result

WADC TR 56-234

from replacement of the =NH group in the amidines by sulfur.

The various compounds prepared in this phase of the work are shown in Table III.

D. 2,4,6 PERFLUOROALKYL 1,3,5 TRIAZINES

The fluorocarbon nitriles, $R_FC\equiv N$, will undergo thermal tri-merization to produce triazines of the following structure:

$$R_F - C \overset{N}{\underset{\underset{\displaystyle R_F}{\overset{\displaystyle |}{C}}}{\underset{N}{\overset{|}{\underset{\displaystyle}{}}}}} \overset{}{\underset{\underset{\displaystyle}{N}}{\overset{\displaystyle}{C}}} - R_F$$
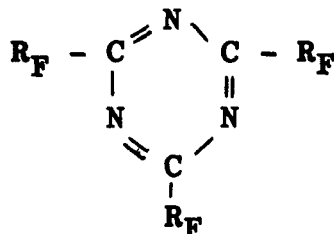
where R_F is CF_3, C_2F_5 or C_3F_7. This type of compound has also been made by a condensation reaction of the perfluoroalkyl amidines involving cyclization of three molecules of the amidine with loss of ammonia. Properties of the perfluoroalkyl s-tria-zines synthesized to date are shown in Table IV.

WADC TR 56-234

18

TABLE III

PROPERTIES OF PERFLUOROALKYL AMIDINES AND RELATED COMPOUNDS

Compound	B.P. °C.	M.P. °C.	d^{25}	n_D^{25}	Nitrogen % Calc.	Nitrogen % Found	Calc.	Found
$CF_3C(:NH)NHCH_3$	47-48 (21 mm)		1.2909	1.3919	22.20	21.85		
$CF_3C(:NH)N(CH_3)_2$	92		1.1795	1.3812	20.01	19.72		
$C_2F_5C(:NH)NHCH_3$	126		1.4258	1.3664	15.91	15.63		
$C_2F_5C(:NH)N(CH_3)_2$	110		1.2969	1.3678	14.75	14.43		
$C_3F_7C(:NH)NHCH_3$	137		1.5140	1.3561	12.37	12.02		
$C_3F_7C(:NH)N(CH_3)_2$	120		1.4242	1.3548	11.66	11.41		
$CF_3C(:NH)NHAg$		200 (dec)			12.71	12.28	48.78[a]	48.40
$C_2F_5C(:NH)NHAg$		240 (dec)			10.36	10.27	40.02[a]	40.38
$C_3F_7C(:NH)NHAg$		277 (dec)			8.74	8.50	33.60[a]	32.88
$(C_2F_5C(:NH)NH)_2Hg$		159 (dec)			10.65	10.22	38.38[a]	38.20
$(C_3F_7C(:NH)NH)_2Hg$		178 (dec)			9.00	8.42	32.31[a]	32.60
$CF_3C(:NH)NH_2.CH_3COOH$		Subl.			16.29	15.94	172[b]	174
$CF_3C(:NH)NH_2.C_3F_7COOH$		Subl.			8.58	8.80	326[b]	323

a. Silver (Mercury) %   b. Neut. Equiv.

TABLE III

PROPERTIES OF PERFLUOROALKYL AMIDINES AND RELATED COMPOUNDS (Continued)

Compound	B.P. °C.	M.P. °C.	d^{25}	n_D^{25}	Nitrogen % Calc.	Nitrogen % Found	Calc.	Found
$C_3F_7C(:NH)NH_2 \cdot CH_3COOH$		Subl.			10.20	10.26	272[b]	277
$C_3F_7C(:NH)NH_2 \cdot C_3F_7COOH$		Subl.			6.58	6.43	426[b]	420
$CF_3C(:S)NH_2$	40 (2 mm)				10.82	10.85	24.78[c]	25.13
$C_2F_5C(:S)NH_2$	60 (23 mm)	39-40			7.82	7.53	17.38[c]	18.13
$C_3F_7C(:S)NH_2$	69 (21 mm)	47-43			6.12	6.01	13.97[c]	13.90

b. Neut. Equiv.   c. Sulfur, %

TABLE IV

2,4,6 PERFLUOROALKYL 1,3,5 TRIAZINES

R_F	b.p., °C.	n_D^{25}	d^{25}	Mol. Wgt. Calc.	Found
CF_3	95.0–96.0	1.3161	1.593	285	288[a]
C_2F_5	121–122	1.3131	1.651	435	431[b]
C_3F_7	164.5–165.0	1.3095	1.716	585	576[b]

a. Victor Meyer Vapor Density

b. Saponification Equivalent

E. REACTION OF PYROLYSIS PRODUCTS OF POLYTETRAFLUOROETHYLENE WITH SULFUR OR SELENIUM

The reaction of polytetrafluoroethylene, or the pyrolysis products produced under the conditions of the experiment, with sulfur or selenium at 500°C under autogenous pressure produced a fusible polymer containing no sulfur or selenium. The melting point of this product is 324–327°C, at which temperature it forms a clear, viscous liquid. Bromination of the product in a sealed tube at 500°C produced a similar polymer with a melting point about 10°C lower than the original product.

Heating tests at 300°C to determine the stability of these polymers in air at elevated temperatures showed little change in the melting points after 37 hours. From 0.7% to 2.4% weight loss was noted after 19 hours at 300°C; little additional weight loss was shown in the remaining 18 hours of heating.

WADC TR 56-234